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Electronic structure and chemical bond in MdO_2

Yury A. Teterin, Mikhail V. Ryzhkov, Andrei E. Putkov, Konstantin I. Maslakov, Anton Yu. Teterin, Kirill E. Ivanov, Stepan N. Kalmykov and Vladimir G. Petrov

Table S1 MO compositions (shares) and energies E_0 [a)](eV) for the MdO_8^{12-} (D_{4h}) cluster at R_{Md-O} = 0.2267 nm and photoemission cross-sections σ_i[b)].

MO		-E_0, eV	MO composition												
			Md										O		
			6s	$6p_{1/2}$	$6p_{3/2}$	$6d_{3/2}$	$6d_{5/2}$	7s	$5f_{5/2}$	$5f_{7/2}$	$7p_{1/2}$	$7p_{3/2}$	2s	$2p_{1/2}$	$2p_{3/2}$
			σ_i 1.29	0.87	1.51	0.63	0.55	0.10	7.68	7.13	0.04	0.06	0.96	0.07	0.07
OVMO	$25\gamma_6^+$	-10.80				0.53	0.34						0.05		0.08
	$22\gamma_7^+$	-10.76				0.49	0.38						0.04	0.02	0.07
	$21\gamma_7^+$	-10.60				0.05	0.83						0.04	0.06	0.02
	$24\gamma_6^+$	-9.05						0.88					0.06	0.02	0.04
	$23\gamma_6^+$	-7.92				0.33	0.53							0.04	0.10
	$20\gamma_7^+$	-7.91				0.33	0.54							0.04	0.09
	$28\gamma_6^-$	-7.45									0.91		0.04	0.03	0.02
	$27\gamma_6^-$	-5.24			0.01							0.91	0.02		0.06
	$24\gamma_7^-$	-5.13										0.91	0.02		0.07
	$23\gamma_7^-$	-0.70							0.03	0.44			0.01	0.22	0.30
	$26\gamma_6^-$ [c)]	0.00								0.62				0.35	0.03
	$22\gamma_7^-$	0.05			0.01				0.01	0.52		0.01	0.01	0.09	0.35
	$25\gamma_6^-$	0.05			0.01				0.01	0.52		0.01	0.01	0.05	0.39
	$24\gamma_6^-$	0.46												0.33	0.67
	$21\gamma_7^-$	0.46												0.33	0.67
	$22\gamma_6^+$	0.73												0.15	0.85
	$19\gamma_7^+$	0.73												0.14	0.86
	$21\gamma_6^+$	0.73												0.66	0.34
	$20\gamma_7^-$	0.90			0.02				0.06	0.34		0.01		0.05	0.52
	$23\gamma_6^-$	0.90			0.02				0.06	0.34		0.01		0.05	0.52
	$18\gamma_7^+$	0.96												0.03	0.97
	$17\gamma_7^-$	1.00												0.50	0.50
	$20\gamma_6^+$	1.00												0.51	0.49
	$19\gamma_7^-$	1.23							0.13	0.37				0.04	0.46
	$22\gamma_6^-$	1.70								0.35	0.02			0.58	0.05
	$21\gamma_6^-$	1.73			0.01				0.02	0.02		0.03		0.21	0.71
	$18\gamma_7^-$	1.73			0.01				0.01			0.03	0.01	0.37	0.57
	$20\gamma_6^-$	2.23								0.01	0.03		0.01	0.23	0.72
	$16\gamma_7^+$	2.38				0.01	0.07						0.01	0.57	0.34
	$19\gamma_6^+$	2.40				0.05	0.03						0.01	0.01	0.90
	$15\gamma_7^+$	2.42				0.04	0.03						0.01	0.36	0.56
	$17\gamma_7^-$	2.47							0.15	0.13		0.01		0.16	0.55
	$19\gamma_6^-$	2.47							0.15	0.12				0.13	0.60
	$16\gamma_7^-$	2.51							0.06	0.19				0.64	0.11
	$18\gamma_6^+$	2.86						0.05					0.01	0.32	0.62
	$14\gamma_7^+$	3.30				0.05	0.08							0.29	0.58
	$18\gamma_6^-$	3.31							0.77	0.01				0.03	0.19
	$15\gamma_7^-$	3.32							0.77	0.01				0.03	0.19
	$17\gamma_6^+$	3.32				0.06	0.08							0.29	0.57
	$14\gamma_7^-$	3.47							0.76					0.04	0.20

IVMO	$17\gamma_6^-$	14.31			0.44							0.03	0.51		0.02
	$13\gamma_7^-$	14.31			0.44							0.03	0.51	0.01	0.01
	$12\gamma_7^-$	15.46							0.01	0.01			0.97		0.01
	$13\gamma_7^+$	15.92					0.05						0.95		
	$16\gamma_6^+$	15.93				0.03	0.02						0.95		
	$12\gamma_7^+$	15.93				0.03	0.02						0.95		
	$16\gamma_6^-$	16.11		0.01							0.04		0.95		
	$15\gamma_6^+$	16.68						0.07					0.93		
	$15\gamma_6^-$	17.99			0.51							0.01	0.46	0.01	0.01
	$11\gamma_7^-$	17.99			0.52								0.46	0.01	0.01
	$14\gamma_6^-$	32.59		0.99											0.01
	$14\gamma_6^+$	57.24	1.00												

[a] Absolute energies are decreased (shifted up) by 18.27 eV.
[b] Photoemission cross-section σ_i (kiloBarn per electron) for O [S1] and for Fm [S2].
[c] Highest occupied MO (1 electron), the number of electrons on the other occupied orbital is 2.

Table S2 Valence XPS parameters for MdO_2 (MdO_8, D_{4h}, $R_{Md\text{-}O}$ = 0.2267 nm) and the Md 6p-, 6d-, 5f-density of states (DOS) ρ_i (e^-).

MO		$-E$[a], eV	XPS Intensity (%)	Md 6p-, 6d-, 5f- DOS ρ_i,(e–)					
				$6p_{1/2}$	$6p_{3/2}$	$6d_{3/2}$	$6d_{5/2}$	$5f_{5/2}$	$5f_{7/2}$
OVMO	26 γ_6^- [c]	6.14	4.10						0.62
	22 γ_7^-	6.19	7.10		0.02			0.02	1.04
	25 γ_6^-	6.19	7.10		0.02			0.02	1.04
	24 γ_6^-	6.60	0.03						
	21 γ_7^-	6.60	0.03						
	22 γ_6^+	6.87	0.03						
	19 γ_7^+	6.87	0.03						
	21 γ_6^+	6.87	0.03						
	20 γ_7^-	7.04	5.50		0.04			0.12	0.68
	23 γ_6^-	7.04	5.50		0.04			0.12	0.68
	18 γ_7^+	7.10	0.03						
	17 γ_7^-	7.14	0.03						
	20 γ_6^+	7.14	0.03						
	19 γ_7^-	7.37	6.80					0.26	0.74
	22 γ_6^-	7.84	4.70						0.70
	21 γ_6^-	7.87	0.60		0.02			0.04	0.04
	18 γ_7^-	7.87	0.20		0.02			0.02	
	20 γ_6^-	8.37	0.60						0.02
	16 γ_7^+	8.52	0.20			0.02	0.14		
	19 γ_6^+	8.54	0.10			0.10	0.06		
	15 γ_7^+	8.56	0.20			0.08	0.06		
	17 γ_7^-	8.61	3.90					0.30	0.26
	19 γ_6^-	8.61	3.80					0.30	0.24
	16 γ_7^-	8.65	3.40					0.12	0.38
	18 γ_6^+	9.00	0.06						
	14 γ_7^+	9.44	0.20			0.10	0.16		
	18 γ_6^-	9.45	11.20					1.54	0.02
	15 γ_7^-	9.46	11.20					1.54	0.02
	17 γ_6^+	9.46	0.20			0.12	0.16		
	14 γ_7^-	9.61	10.90					1.52	
	$\Sigma I_i,\rho_i$[b]		87.80		0.16	0.42	0.58	5,92	6.48

IVMO	17 γ_6^-	20.45	1.50		0.88				
	13 γ_7^-	20.45	1.50		0.88				
	12 γ_7^-	21.60	0.70					0.02	0.02
	13 γ_7^+	22.06	1.80				0.10		
	16 γ_6^+	22.07	0.50			0.06	0.04		
	12 γ_7^+	22.07	0.50			0.06	0.04		
	16 γ_6^-	22.25	0.40	0.02					
	15 γ_6^+	22.82	0.40						
	15 γ_6^-	24.13	1.60		1.02				
	11 γ_7^-	24.13	1.70		1.04				
	14 γ_6^-	38.73	1.60	1.98					
	$\Sigma I_i,\rho_i$ [b)]		12.20	2.00	3.82	0.12	0.18	0.02	0.02
	14 γ_6^+	63.38	~ 2.4						

[a)] Absolute energies are increased (shifted down) by 6.14 eV.
[b)] Peak intensities and partial densities of states.

Table S3 Overlap populations for MdO_2 (per one ligand, $\times 10^3$).

Bonds in MdO_2			RDV	Bonds in MdO_2			RDV
Md $5f_{5/2}$	–	O 2p	-3	Md $6d_{3/2}$	–	O 2s	17
Md $5f_{7/2}$	–	O 2p	15	Md $6d_{5/2}$	–	O 2s	26
Md $5f_{5/2}$	–	O 2s	-2	$\Sigma^{a)}_{OVMO}$			348
Md $5f_{7/2}$	–	O 2s	0				
Md $7p_{1/2}$	–	O 2p	21	Md $6p_{1/2}$	–	O 2p	-11
Md $7p_{3/2}$	–	O 2p	46	Md $6p_{3/2}$	–	O 2p	-66
Md $7p_{1/2}$	–	O 2s	12	Md $6p_{1/2}$	–	O 2s	-2
Md $7p_{3/2}$	–	O 2s	9	Md $6p_{3/2}$	–	O 2s	-22
Md 7s	–	O 2p	24	Md 6s	–	O 2p	-15
Md 7s	–	O 2s	20	Md 6s	–	O 2s	-1
Md $6d_{3/2}$	–	O 2p	67	$\Sigma^{a)}_{IVMO}$			-117
Md $6d_{5/2}$	–	O 2p	96	$\Sigma^{a)}_{MO}$			231

[a)] OVMO, IVMO and CMO contributions.

References

S1 J. H. Scofield, *J. Electron Spectrosc. Relat. Phenom.*, 1976, **8**, 129; https://doi.org/10.1016/0368-2048(76)80015-1

S2 V. G. Yarzhemsky, A. Yu. Teterin, Yu. A. Teterin and M. B. Trzhaskovskaya, *Nucl. Technol. Radiat. Prot.*, 2012, **27**, 103; https://doi.org/10.2298/NTRP1202103Y.